

SNOOK

The use of Barium Salts

in Water Treatment.

The Application of the Hydrogen

Electrode in Water Analysis

Chemical Engineering

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**THE USE OF BARIUM SALTS
IN WATER TREATMENT.
THE APPLICATION OF THE HYDROGEN
ELECTRODE IN WATER ANALYSIS.**

BY

JOHN DONALD SNOOK

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1915



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June 2, 1915.

Dean K. C. Babcock,
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Dear Sir:

I hope you can accept the thesis of Mr. J. D. Snook.
Mr. Snook had expected to have it copied but was unable
to get someone to do it and attempted to copy it himself.
Because of the many tables it took longer than he expected
and it therefore was not entirely ready on time. Furthermore,
Mr. Snook did not realize that it was due at noon

June 1.

Approved
W. A. Noyes

Very truly yours,

Edward Bartow
6/2/15 - 3 pm.

Edward Bartow

Professor Sanitary Chemistry

EB/CHS

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UNIVERSITY OF ILLINOIS

JUNE 1, 1915

191

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

JOHN DONALD SNOOK

ENTITLED THE USE OF BARIUM SALTS IN WATER TREATMENT.

THE APPLICATION OF THE HYDROGEN ELECTRODE IN WATER ANALYSIS.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

Edward Bartow

Instructor in Charge

APPROVED:

W. A. Noyes

HEAD OF DEPARTMENT OF

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310227

THE USE OF BARIUM SALTS
IN
WATER TREATMENT.

All natural waters contain impurities, the amount of which depends upon the nature of the soil through which the water has passed. When these impurities are present in sufficiently large amounts, it is necessary to remove them before the water can be used satisfactorily for certain industrial purposes. The most important of these is its use in steam boilers. When a hard water is used in a steam boiler, the impurities are deposited and form crusts which are more or less hard and adherent.* These crusts

*W. H. Booth, Water Softening and Treatment, London, 1906.

have a low heat conductivity and so lower the efficiency of the boiler, and considerable time and expenditure is required to remove the encrustation. This inconvenience and expense may be avoided by using initially pure water, or water from which the impurities have been removed in some way. Since only a small part of the natural waters are sufficiently pure, the softening of water for use in boilers is very important.

Pure water is also necessary, or beneficial, in many manufacturing processes, particularly in the preparation of high grade fabrics,* the dyeing of fine wools, in brewing, in drug

*W. Kind. Seifensieder Ztg., 40,69.

extracts, and in cleaning and washing purposes.

The methods for softening water may be divided into two classes, namely, those which remove the impurities by the aid of heat, and those which use chemical means. In the first class various kinds of heaters are used for heating the water before it is used. The carbon dioxide is driven off by the heat, and the carbonates of calcium and magnesium are precipitated. In the second class there are a number of reagents used, and a great many forms of apparatus for carrying on the treatment. Some of the reagents used are as follows:

Lime, or calcium hydroxide, is the reagent most generally used. This method was first proposed by Dr. Clark in England about 1856.* It precipitates the bicarbonates of calcium and

*W. W. Christie, Boiler Waters, New York, 1906, 177.

magnesium as the carbonate and hydroxide respectively.

Sodium carbonate is used to remove the sulphates of calcium and magnesium, since it precipitates these as the carbonates. This is often used with lime or with heaters, since these do not remove the permanent hardness.

Sodium hydroxide removes the bicarbonates of calcium and magnesium, and the sodium carbonate formed removes the calcium and magnesium sulphates. However, this is not used to any extent, on account of the high cost of the reagent.

Barium carbonate precipitates any sulphates present in the water as the very insoluble barium sulphate.

Barium hydroxide removes the sulphates of calcium and magnesium, and the calcium and magnesium hydroxides formed

precipitate the bicarbonates. These reactions may be considered in the reverse order, that is, that the barium hydroxide first reacts with the bicarbonates and the barium carbonate thus formed precipitates the sulphates.*

*H. de LaCoux, L'Eau L'Industrie, 1900, 71.

Permutit, an artificially prepared aluminate silicate, having the formula $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 3\text{Na}_2\text{O} \cdot 6\text{H}_2\text{O}$, replaces the calcium and magnesium by sodium, simply by filtering the water through it.*

*T. R. Duggan, Orig. com. 8th Intern. Congr. Appl. Chem. (Appendix), 25, 125.

Since this is to be a study of the use of barium salts, these methods will be described more in detail.

Barite, or heavy spar, is the principal source of barium compounds. This is the natural sulphate of barium and is commonly called barytes. It is a common mineral of wide distribution, and usually occurs as a gangue material in metallic veins, associated especially with ores of silver, lead, copper, cobalt, manganese and antimony. It sometimes occurs in veins in limestone with calcite and celestite, or in sandstone with copper ores. Occasionally it is deposited as a sinter by hot springs. Notable localities for the occurrence of crystalline barite are in Westmorland, Cornwall, Cumberland, Derbyshire and Surrey, England; Felsőbanya and other localities in Hungary; in Saxony, and in Bohemia.*

*J. D. Dana, Manual of Mineralogy, New York, 1913, 300.

In the United States it is found at Cheshire, Connecticut; DeKalb, New York; and Fort Wallace, New Mexico. Massive barite, occurring usually as veins, nests and irregular bodies in limestone, is quarried in Nova Scotia, Missouri, and the Appalachian states. In 1913 over 68 per cent of the total output of the United States came from Missouri, while among the Appalachian states, Georgia, North Carolina, Tennessee, South Carolina and Virginia are in the order of their importance.*

*J. M. Hill, Mineral Resources of the United States, United States Geological Survey, 1913, 169.

Barite is usually a white opaque to translucent crystalline material, with a vitreous luster, about as hard as calcite, but it differs from calcite in its greater specific gravity. It has a hardness of 3 to 3.5, and a specific gravity of 4.5, which is heavy for a nonmetallic mineral.*

*J. D. Dana, Manual of Mineralogy, New York, 1913, 300.

Natural barite is rarely pure, its most common impurities being silica, lime, magnesia, and the oxides of iron and aluminium. Fine particles of galena are disseminated through many of the deposits in the United States. The commercial grades of the mineral as mined carry from 95 to 98 per cent barium sulphate, and 1 to 3 per cent silica.

The mineral is ground and sometimes purified by washing, and then used as a partial substitute for white lead in paint, as a base in the manufacture of lake pigments, to give weight to

paper and cloth, in the manufacture of white rubber goods, of asbestos cement, of artificial ivory, and in the preparation of fertilizers, boiler compounds, insecticides, hydrogen peroxide, and artificial driftwood salts.*

*J. M. Hill, Min. Res. of U. S., U. S. Geol. Survey, 1913, 168.

Barium oxide is made commercially by heating barite and carbon in the electric furnace. When this is dissolved in water the hydroxide is formed.

A minor source of barium is the natural carbonate, witherite. It is found as fine crystals at Hexham in Northumberland, and Alston Moor in Cumberland. It also occurs at Tarnowitz in Silesia; Leogang in Salzburg; near Lexington, Kentucky; and Thunder Bay, Lake Superior.* It does not occur in large enough

*J. D. Dana, Manual of Mineralogy, New York, 1913, 216.

quantities, however, to be of very great importance.

When any soluble salt of barium is added to a water containing sulphates, barium sulphate is precipitated, since its solubility is only 2.3 milligrams per liter at 19° Centigrade.*

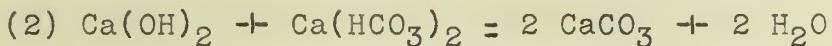
*Z. physik. Chem. 12, 131, 241, 1893.

If the carbonate, which is slightly soluble, is used the reaction is shown by the equation:



Since the calcium carbonate formed is also very insoluble, it also precipitates.

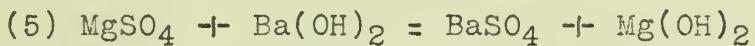
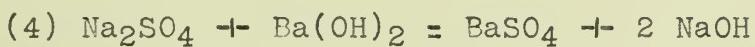
If the hydroxide is added to a water containing the bicarbonate and sulphate of calcium, the reactions which take place are as follows:



*H. de LaCoux, L'Eau L'Industrie, 1900, 71.

As shown in equation (1), the barium hydroxide reacts with the calcium sulphate giving the insoluble barium sulphate and calcium hydroxide, which reacts with the calcium bicarbonate, causing both to be precipitated as carbonates, as shown in equation (2). The excess bicarbonate will react directly with barium hydroxide, according to equation (3), and the carbonates will be precipitated.

Sodium, potassium, or magnesium salts react in a similar manner with barium hydroxide.



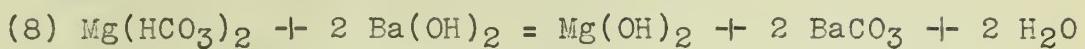
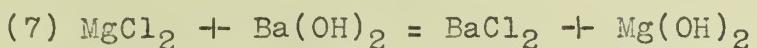
The sodium hydroxide formed in the reaction shown in equation (4) will react with any magnesium salts present, giving the insoluble magnesium hydroxide.



When the barium hydroxide reacts with magnesium sulphate, as shown in equation (5), both of the products are precipitated.

If no sodium or potassium sulphates are present, the barium hydroxide will react directly with the magnesium chloride

or bicarbonate, precipitating it as the hydroxide.



From these equations it is evident that when barium carbonate is used, the sulphates only are removed, so that if it is desired to remove the temporary hardness also, some other reagent must be used for this purpose.

The hydroxide, besides precipitating the sulphates, removes an equivalent amount of bicarbonates. When the bicarbonates are in excess of the sulphates, the excess may be removed by using a sufficiently large amount of barium hydroxide, or just enough may be used to precipitate the sulphates, and the excess bicarbonates removed by some other reagent.

EXPERIMENTAL PART

A number of experiments have been made in the chemical laboratory of the University of Illinois to determine the effect produced by treating a hard water with barium salts, and with lime and barium salts. For each treatment 16 samples of 2 liters each were treated with varying amounts of the reagents. Water from a well at the Cunningham Children's Home, one mile northeast of Urbana, was used. The barium hydroxide was dissolved in distilled water and added to the samples immediately, since the carbon dioxide of the air precipitates some of the barium from the solution as the carbonate in a short time. On account of the insolubility of the barium carbonate and lime, separate portions of these reagents were weighed out for each sample. After treatment the samples were allowed to stand in stoppered bottles for several days, with frequent shaking. They were then filtered through paper, and the following tests were made on the filtered water:

- (1) Non-carbonate Hardness
- (2) Magnesium as CaCO_3
- (3) Alkalinity
- (4) Calcium
- (5) Sulphate
- (6) Chlorine
- (7) Barium
- (8) Residue on Evaporation

The methods used for making these tests are as follows:

(1) "Determination of Non-carbonate Hardness. 200 cc. of the water are put into a 500 cc. Erlenmeyer flask and boiled for 15 minutes to expel the CO_2 . Then 25 cc. of N/20 soda reagent, - a mixture of equal parts of NaOH and Na_2CO_3 , - are added, boiled 10 minutes, and filtered into a 200 cc. volumetric flask. In an aliquot portion the excess of alkali is titrated with N/50 H_2SO_4 , using methyl orange as an indicator. A blank determination is also made using distilled water.

"The difference between the number of cc. used for the blank and the number of cc. used for the water is the non-carbonate hardness (N. C. H.) in terms of CaCO_3 . If the water contains sodium carbonate, the number of cc. used for the blank determination will be less than that used for the water.

(2) "Determination of Magnesium. Rapid Method. 100 cc. of the water (the portion in which the alkalinity was determined may be used) is neutralized carefully with N/50 H_2SO_4 to methyl orange in a 200 cc. volumetric flask, and heated on a hot plate to expel the CO_2 . 25 or 50 cc. of saturated lime water are added. This is allowed to stand on a water bath for about 15 minutes, to allow the precipitate to settle completely. It is then made up to about 5 cc. above the mark with distilled water to allow for contraction, shaken thoroughly and allowed to cool. The excess of lime is determined by titrating an aliquot portion of the supernatent liquid or filtrate with N/50 H_2SO_4 , using methyl orange as an indicator.

"At the same time a blank of distilled water is treated in the same way. The difference in the volume of acid used for

the blank and for the water represents the amount of magnesium present in terms of CaCO_3 .

(3) "Determination of Alkalinity. Several drops of phenol phthalein are added to 100 cc. of the water, and if there is a coloration, N/50 H_2SO_4 is added until the color disappears. A few drops of methyl orange are then added and H_2SO_4 added until the color changes."

(4) Determination of Calcium. 500 cc. of the water, which had been made acid with HCl, are evaporated to about 100 cc. NH_4OH is added until the solution is alkaline. Ammonium oxalate is then added in excess. After standing for some time the clear liquid is poured through a filter, and the precipitate washed in the beaker with hot water. The precipitate on the filter is removed by allowing warm dilute sulphuric acid to pass through it several times. This is added to the precipitate in the beaker. To this turbid solution, 20 cc. of sulphuric acid (1:1) are added, and after dilution with hot water to about 300 cc., the oxalic acid was titrated with N/20 KMnO_4 solution.

(5) Determination of Sulphate. To 100 cc. of the boiling water, which has been added enough HCl to make it acid, an excess of hot barium chloride solution is added drop by drop. It is allowed to stand on the hot plate until the precipitate settles readily, and then is allowed to stand for some time. The precipitate is then filtered off, washed, ignited and weighed as barium sulphate.

(6) Determination of Chlorine. This is determined by titrating 100 cc. of the water with silver nitrate solution,

using potassium chromate as an indicator.

(7) Determination of Barium. 500 cc. of the water, which has been acidified with HCl, are evaporated to about 100 cc., and 25 cc. of hot saturated calcium sulphate solution added drop by drop to the boiling water. After standing for some time, the precipitate is filtered off, washed, ignited and weighed as barium sulphate.

(8) "Determination of Residue on Evaporation. 100 cc. of the water is evaporated to dryness on the steam bath in a weighed platinum dish. The residue is then dried for an hour in an oven at a temperature of about 170° Centigrade, and when cool is weighed.

A number of determinations of barium were made in waters to which known amounts of a barium salt had been added, in order to test the accuracy of the method. The results obtained are given below:

I. 10 milligrams of barium as the chloride were added to 100 cc. of distilled water, and the barium determined by the method already given. The results were as follows:

	BaSO ₄	Ba
1	17.5	10.3
2	16.8	9.9
3	17.1	10.1
4	17.3	10.2
5	16.7	9.8
6	17.3	10.2

II. 10 milligrams of barium were added to 100 cc. distilled water, as in I.

	BaSO ₄	Ba
1	16.6	9.8
2	17.2	10.1
3	17.5	10.3
4	16.8	9.9
5	17.0	10.0
6	16.5	9.7

III. 10 milligrams of barium were added to 500 cc. of the University tap water, and this was evaporated to about 100 cc. The barium was determined as before.

	BaSO ₄	Ba
1	17.3	10.2
2	17.1	10.1
3	16.5	9.7
4	16.9	10.0
5	16.6	9.8
6	16.8	9.9

IV. 10 milligrams of Parium were added to a liter of the University tap water, and this was evaporated to about 100 cc.

	BaSO ₄	Ba
1	17.2	10.1
2	16.7	9.8
3	16.8	9.9
4	17.5	10.3
5	16.8	9.9
6	17.3	10.2

V. Barium as the chloride was added in varying amounts to a liter of the University tap water, and this was evaporated to about 100 cc.

	Ba added	BaSO ₄	Ba
1	10 mg.	17.3	10.2
2	10 "	16.8	9.9
3	20 "	33.4	19.7
4	20 "	34.1	20.1
5	30 "	51.3	30.2
6	30 "	50.2	29.6

These results show that for small amounts of barium the method can be relied upon to give results which are within .3 milligram of the correct value. This was sufficiently accurate for this purpose, so the method was used in determining the barium in the treated water.

To be certain that there was no barium in the untreated water, a small amount of it was evaporated to dryness, the residue taken up in hydrochloric acid, and tested by the spectroscope. There was no evidence of barium.

The water which was treated with barium salts was obtained from a 60 foot drilled well at the Cunningham Children's Home, one mile northeast of Urbana. For the first treatment 16 samples of 2 liters each were measured out and put in glass stoppered bottles. To these were added varying amounts of a freshly prepared solution of barium hydroxide. The samples were allowed to stand for several days with frequent shaking, and were then filtered through paper and the filtrate analysed according to the methods already given. The results obtained are given in the following table:

TABLE I
Sample Ba(OH)₂8aq N.C.H. Mg as CaCO₃ Alkalinity Calcium Sulphate Chlorine Barium Residue
Ph ph m.o.

1	00	86	176	0	411	126	96.6	13	0	567
2	100	52	136	0	361	108	57.5	13	.7	484
3	200	30	124	0	317	90	40.3	13	1.2	419
4	300	16	104	0	285	78	18.9	13	1.7	365
5	400	8	92	0	264	71	5.8	13	6.6	338
6	500	4	88	0	255	68	4.9	13	19.0	327
7	700	6	92	0	245	63	5.0	13	18.6	292
8	900	6	88	0	220	55	4.9	13	12.7	261
9	1100	4	84	2	214	53	4.8	13	7.7	232
10	1300	0	76	16	195	42	4.5	13	4.7	187
11	1400	6	64	19	165	34	4.5	13	4.5	174
12	1500	4	60	20	154	30	4.3	13	4.3	165
13	1600	4	52	20	140	28	4.5	13	4.1	145
14	1700	6	48	19	125	25	4.2	13	4.2	131
15	1800	2	40	20	115	23	4.0	13	4.1	125
16	2000	4	28	27	105	20	4.1	13	4.0	118

By calculating from the data in Table I, the content of the samples was found to be as given in the following table:

TABLE II

Sample	NaCl	Na ₂ SO ₄	MgSO ₄	MgCO ₃	CaCO ₃	Barium
1	21.5	30.0	96	81	315	0
2	21.5	21.3	54	76	270	.7
3	21.5	13.6	39	77	225	1.2
4	21.5	7.8	17	75	195	1.7
5	21.5	1.5	6	73	177	6.6
6	21.5	2.5	4	71	170	19.0
7	21.5	1.5	5	74	157	18.6
8	21.5	.2	6	70	137	12.7
9	21.5	1.2	5	67	132	7.7
10	21.5	4.3	2	62	105	4.7
11	21.5	1.9	4	51	85	4.5
12	21.5	5.2	1	50	75	4.4
13	21.5	4.3	2	42	70	4.1
14	21.5	.3	5	37	62	4.2
15	21.5	3.5	2	32	57	4.1

Treatment II. The same water was used for the second treatment as for the first, and 16 2 liter samples were used. Lime and barium carbonate were added in varying amounts, each portion being weighed and added in the solid form. After standing for several days with frequent shaking, the samples were filtered and analysed as in the first treatment. The results are shown in the following table:

TABLE III

Sample $\text{Ca}(\text{OH})_2$ BaCO_3 N.C.H. Mg as CaCO_3 Alkalinity Ph ph m.O.

1	00	00	82	172	0	415	128	96.9	13	0	572
2	50	25	70	160	0	384	117	84.6	13	.7	507
3	100	50	62	148	0	357	106	72.6	13	.8	463
4	150	75	52	136	0	295	82	65.1	13	.8	396
5	200	100	46	132	0	258	68	58.8	13	.9	352
6	250	125	40	124	3	191	41	50.5	13	1.0	261
7	300	150	34	116	9	154	24	44.1	13	.9	210
8	350	175	24	112	18	159	22	36.5	13	1.1	207
9	400	200	20	108	20	157	20	30.9	13	1.1	195
10	450	225	18	104	27	160	19	25.8	13	1.3	163
11	500	250	16	100	44	174	18	19.3	13	1.7	152
12	550	275	12	96	71	199	18	16.1	13	2.6	149
13	600	300	8	60	102	202	18	10.7	13	7.9	155
14	650	325	4	36	147	264	17	6.2	13	10.5	170
15	700	350	4	28	198	360	15	3.7	13	12.0	196
16	750	375	2	24	246	452	14	2.9	13	12.6	243

Calculating from the data in Table III, the content of the filtered samples from the second treatment was found to be as given in the following table:

TABLE IV

Sample	NaCl	Na ₂ SO ₄	MgSO ₄	MgCO ₃	CaCO ₃	Barium
1	21.5	33.9	93	80	320	0
2	21.5	29.0	82	77	292	.7
3	21.5	27.5	67	77	265	.8
4	21.5	31.2	55	76	205	.8
5	21.5	24.9	53	74	170	.9
6	21.5	20.0	47	71	103	1.0
7	21.5	20.8	37	71	60	.9
8	21.5	17.0	31	72	55	1.1
9	21.5	16.1	25	73	50	1.1
10	21.5	13.0	22	72	47	1.3
11	21.5	7.8	18	71	45	1.7
12	21.5	6.1	16	70	45	2.6
13	21.5	4.4	10	44	48	7.9
14	21.5	.6	7	25	87	10.5
15	21.5	0	5	20	138	12.0
16	21.5	1.5	2	18	184	12.6

Residue
P.P.M.
600

Residue
on
Evaporation
II

400

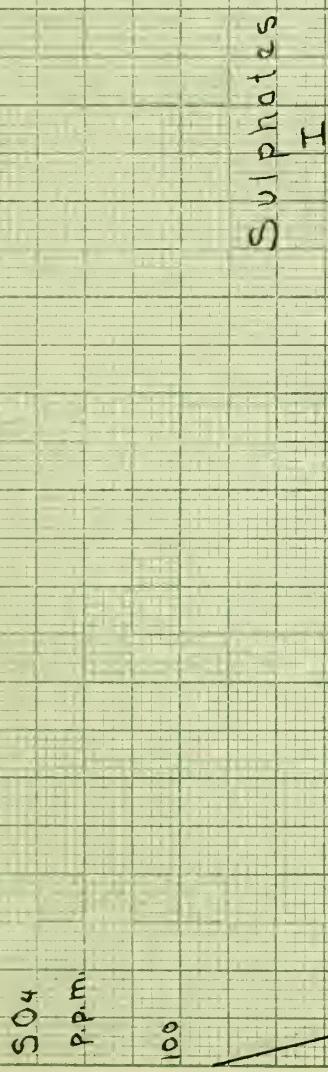
200

1500

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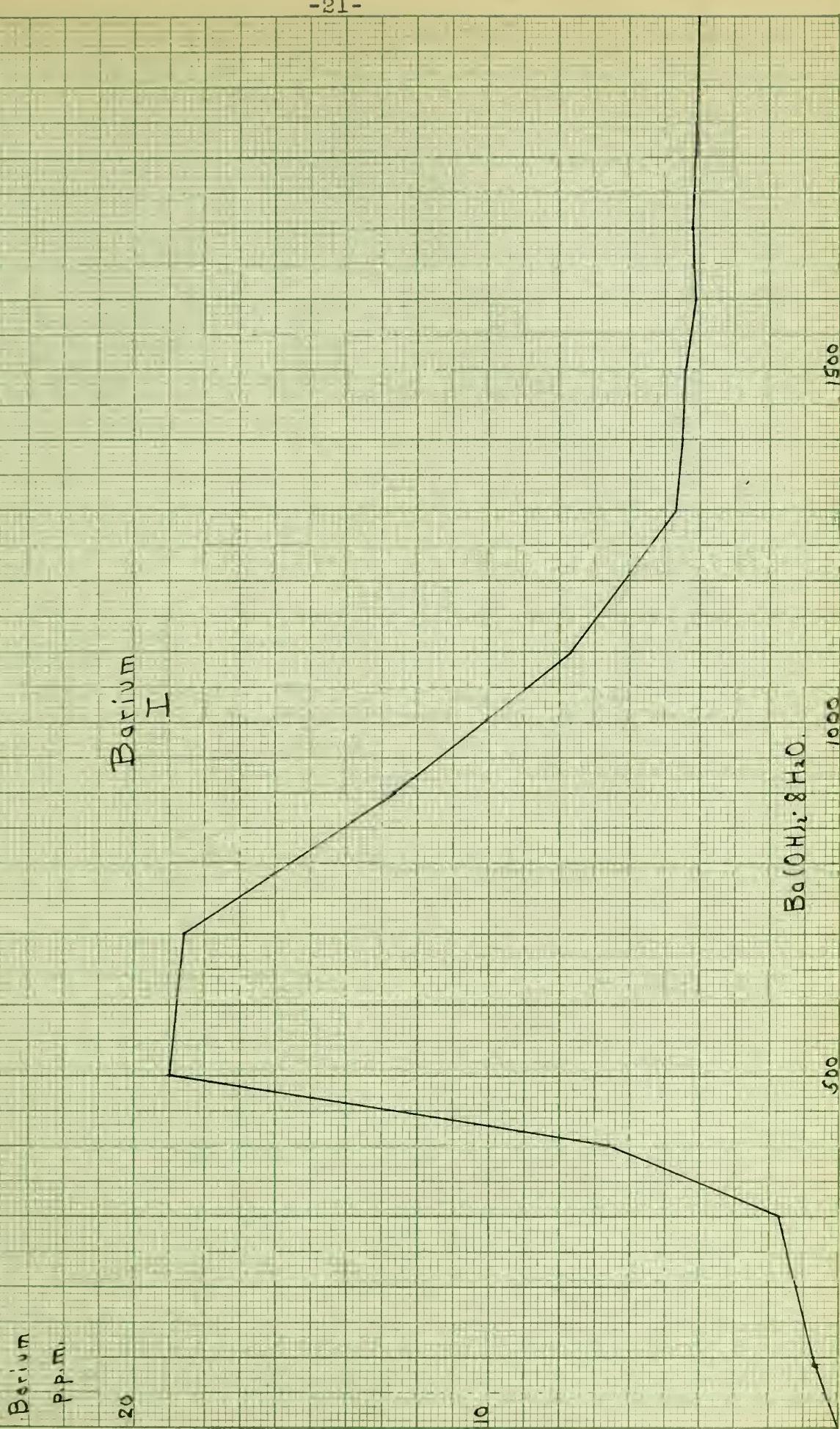
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ P.P.M.



Ba(OH)₂: 8 H₂O, P.P.M.

1500

500



Residue
P.P.M.
600

Residue
on
Evaporation
II

400

200

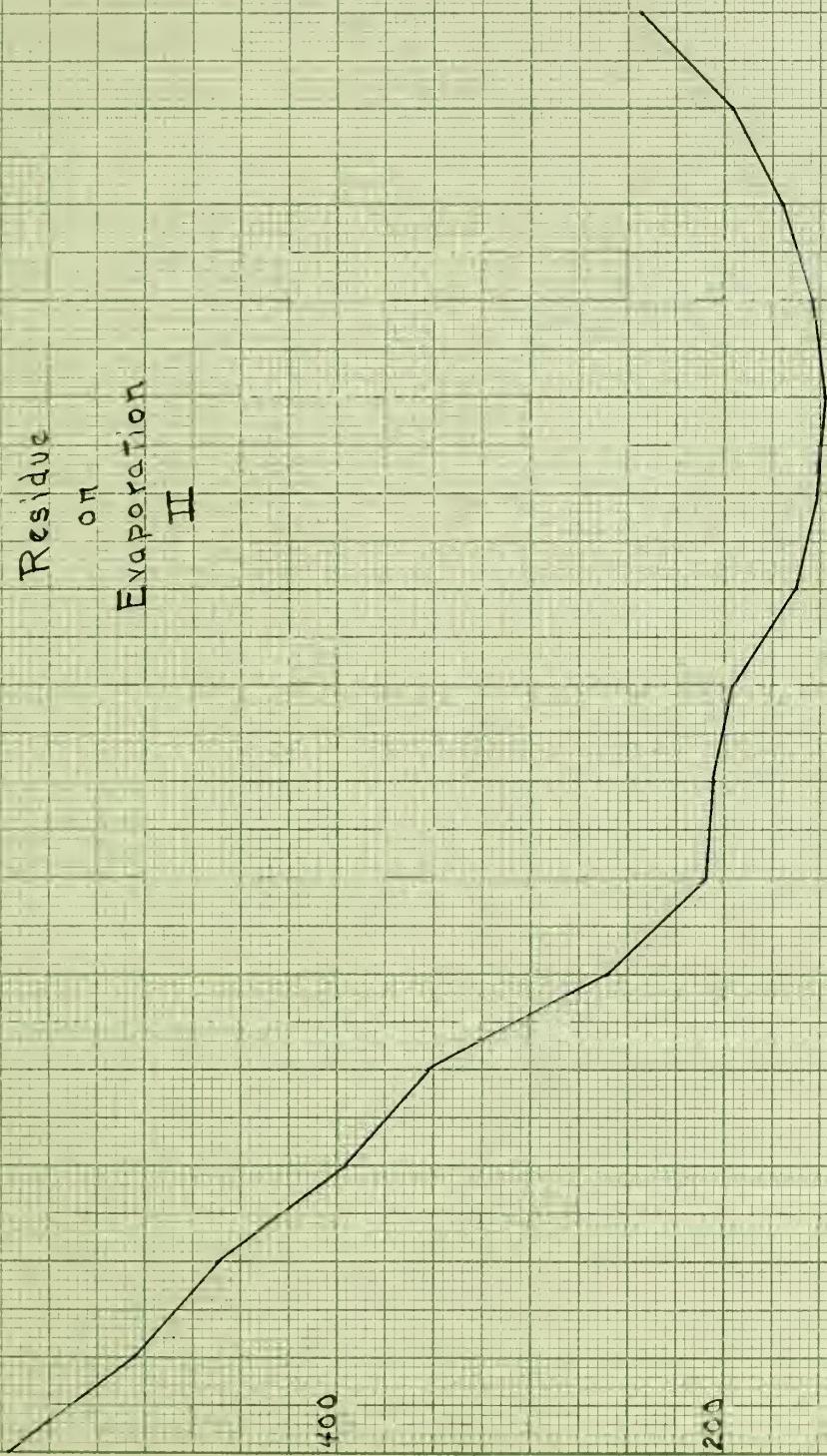
BaCO_3
 Ca(OH)_2

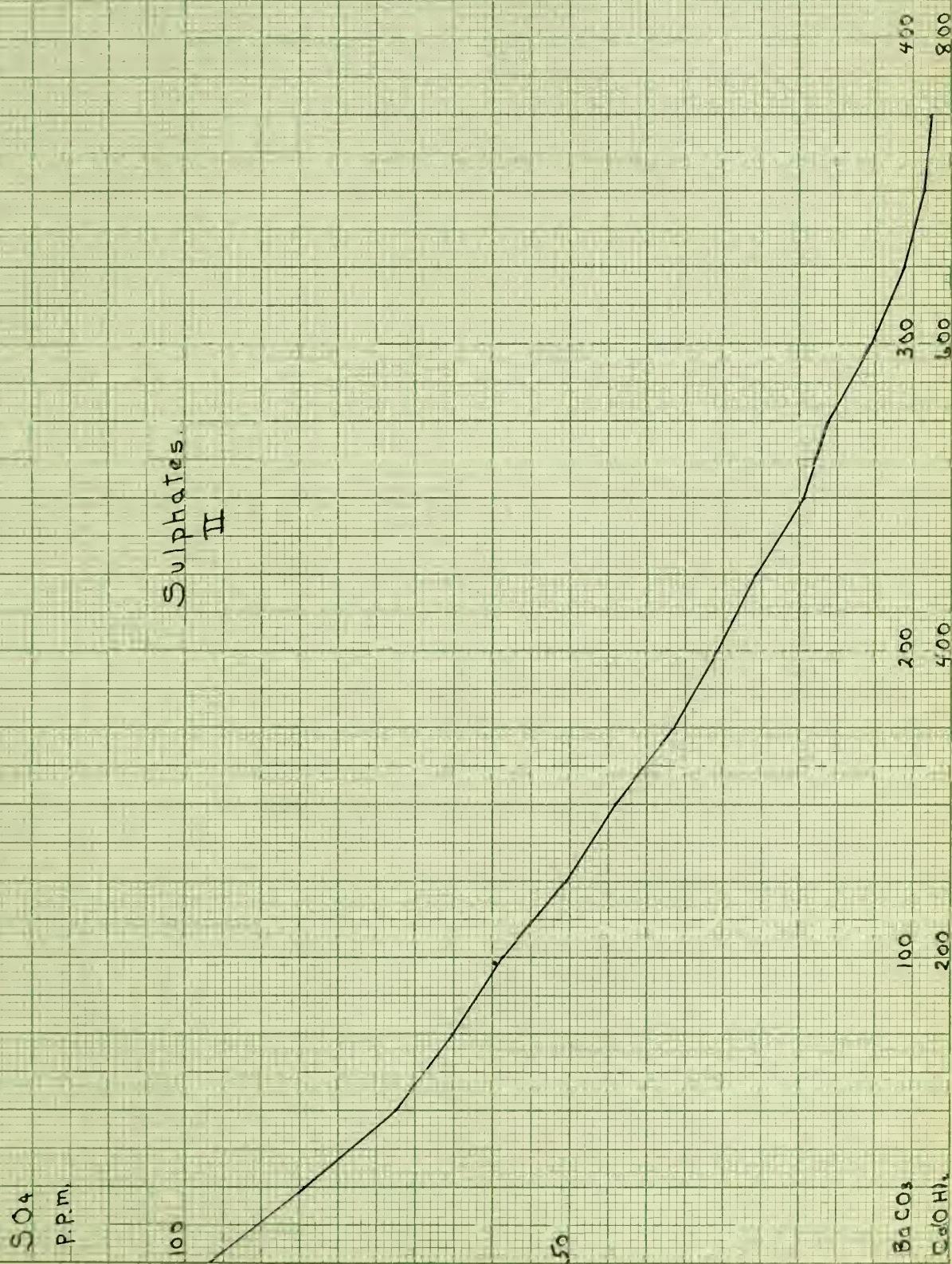
100
200

300
400

500
600

700
800





Barium
III

P.P.M.

12

8

4

250
500
125
250

BaCO_3 - P.P.M.
 Ca(OH)_2 - g/m.

From these results it is seen that barium hydroxide and carbonate are very satisfactory reagents for removing the permanent hardness of a water. In both treatments the sulphate was reduced as low as 4 parts per million. Not only the sulphates of calcium and magnesium, but sodium sulphate as well, were removed. This is a decided advantage over sodium carbonate, which gives a larger amount of sodium sulphate in the treated water than was in the untreated water.

Barium carbonate is a convenient reagent to use, for, on account of its slight solubility, a large amount can be put in the softening apparatus, and there is no danger of overtreatment. When the hydroxide is used, it is necessary to limit the amount since any excess would remain in the water.

When the hydroxide is used, the effect on the bicarbonates is similar to that obtained by using lime. In fact, they are partially removed by the calcium and magnesium hydroxides which are formed when the sulphates are precipitated. The remainder of the bicarbonates is in a large part removed by more barium hydroxide.

The removal of the sulphates from this water by means of the hydroxide would cost about $6\frac{1}{2}$ cents per thousand gallons, while it would cost 22 cents if enough were used to remove the bicarbonates. The cost of removing the sulphates with barium carbonate would be about 5 cents per thousand gallons, and with the lime would be 7 cents.

Some objection has been made to the use of barium salts for water treatment, because they are poisonous. It is true

that the salts of barium, with the exception of the sulphate, are rapidly acting heart stimulants, and when taken in sufficiently large quantity cause death in a short time. The fatal dose of the chloride is 10 to 15 grams.* The carbonate is also toxic,

*Schweiz. Wochschr. 50, 419.

but acts more slowly. These salts do not seem to be very accumulative, except in cases where there is a lack of calcium in the diet, and then most of it is found in the bones. Experiments were made along this line by C. L. Alsberg and O. F. Black.* Half grown rats were fed for some months on a mixed diet

*Proc. Soc. Exp. Biol. Med. 9, 37.

to which barium sulphate had been added. They remained in good health and did not store up measurable amounts of barium in their tissues. When, however, the animals were fed on a diet poor in calcium, a few milligrams of barium were stored in the tissues of each animal. As much as 200 milligrams of barium chloride has been prescribed for children, to be taken three times a day, when used as a remedy for scrofula.

The largest amount of barium found in any of the samples treated was 19 milligrams per liter, and as far as is known, this amount would produce no harmful effects if the water were used for drinking purposes.

The only objection of any importance that could be made to the use of barium salts is their cost. If a cheaper method could be found for preparing the salts, they would be very satisfactory reagents for use in water treatment.

THE APPLICATION OF THE HYDROGEN ELECTRODE
IN
WATER ANALYSIS

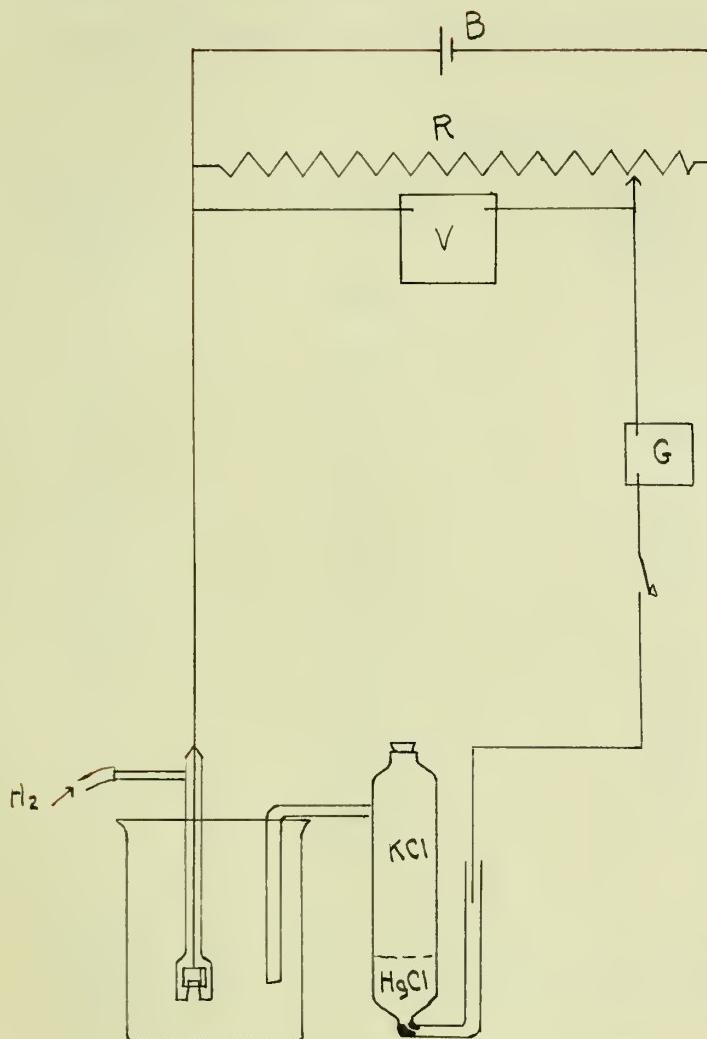
The hydrogen electrode was used in making several titrations, to determine whether this method could be used for determining the alkalinity and magnesium content of a water.

The apparatus used is shown in the accompanying sketch. The hydrogen electrode consists of a small piece of platinized platinum foil, over which hydrogen is bubbling slowly. The calomel electrode used consists of a layer of mercurous chloride with a little metallic mercury, and a solution of potassium chloride.

The water to be titrated was placed in a beaker and the hydrogen electrode and the side arm of the calomel electrode placed in it. A small amount of the solution, which was being used in the titration, was added at intervals and the voltage read, after the resistance had been adjusted so that the galvanometer showed a balance. These readings were plotted on coordinate paper and the inflection point on the curve was taken as the end point.

In these titrations the alkalinity was first determined by neutralizing with .02 normal sulphuric acid, and adding a little in excess. This acid was added in small quantities, and a reading was taken after each addition.

The solution was then boiled to remove the carbon dioxide, and titrated in a similar manner with .01 normal sodium hydroxide.



According to Mr. Hildebrand,* the excess acid would first be

*J. H. Hildebrand, J. A. C. S. 35, 867.

neutralized, giving an inflection point when neutral and another when the magnesium was all precipitated, at the point where the calcium began to come down.

The readings and curves obtained are as follows:

TITRATION I

Volume H ₂ SO ₄	Voltage	Volume H ₂ SO ₄	Voltage
0	.748	33	.484
5	.679	34	.453
10	.624	34 $\frac{1}{4}$.435
15	.584	34 $\frac{1}{2}$.430
20	.563	34 $\frac{3}{4}$.421
25	.538	35	.415
30	.516	35 $\frac{1}{4}$.410
31	.502	35 $\frac{1}{2}$.407
32	.490	36	.404

Alkalinity from curve - 34.3 cc. or 343 p.p.m.

Alkalinity from titration using methyl orange - 342 p.p.m.

TITRATION II

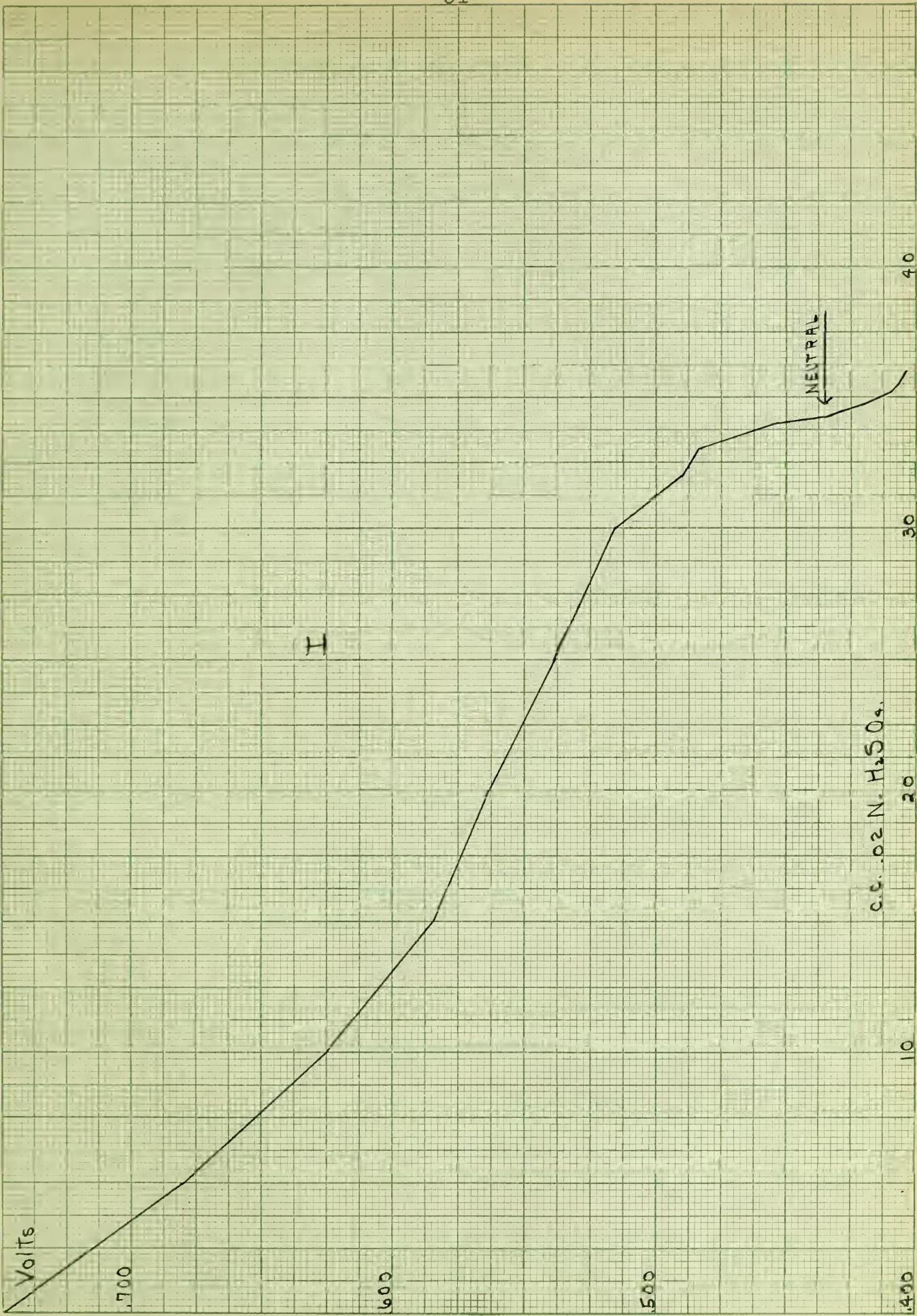
Volume H ₂ SO ₄	Voltage	Volume H ₂ SO ₄	Voltage
0	.743	33	.480
5	.681	33½	.476
10	.628	34	.464
15	.591	34¼	.437
20	.566	34½	.420
25	.530	34¾	.414
30	.494	35	.410
31	.489	35½	.406
32	.486	36	.402

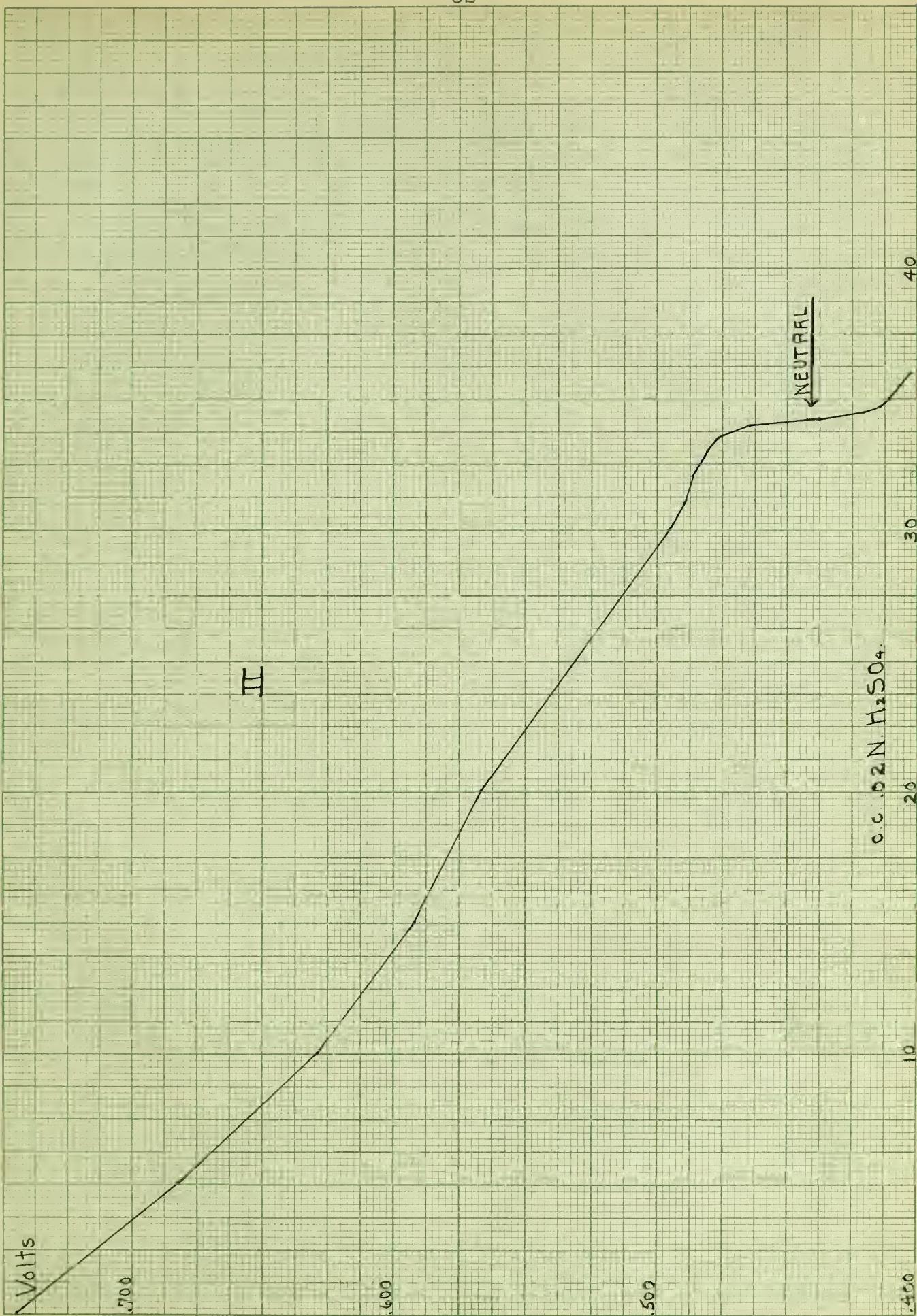
Alkalinity from curve - 34.2 cc. or 342 p.p.m.

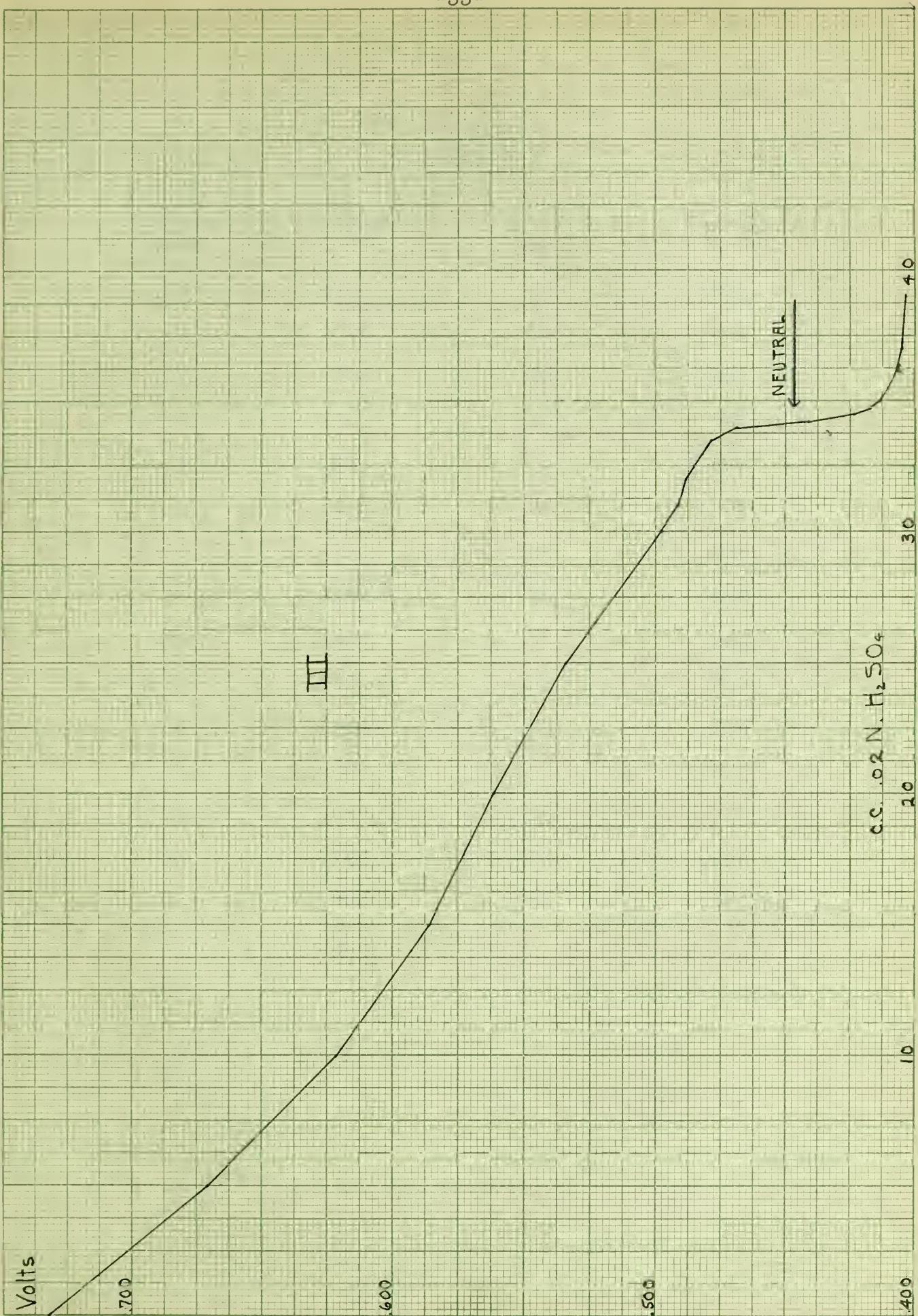
TITRATION III

Volume H ₂ SO ₄	Voltage	Volume H ₂ SO ₄	Voltage
0	.732	33½	.478
5	.670	34	.468
10	.621	34¼	.441
15	.586	34½	.423
20	.561	34¾	.417
25	.534	35	.413
30	.497	35½	.410
31	.491	36	.407
32	.488	37	.405
33	.481	39	.403

Alkalinity from curve - 34.2 cc. or 342 p.p.m.







TITRATION IV

Volume NaOH	Voltage	Volume NaOH	Voltage
0	.478	16	.831
1	.504	17	.843
2	.526	18	.861
3	.541	20	.871
4	.570	25	.890
5	.591	30	.893
6	.611	35	.902
7	.652	40	.912
8	.672	45	.912
9	.690	50	.912
10	.704	55	.912
11	.726	60	.917
12	.747	65	.917
13	.765	75	.917
14	.791	90	.925
15	.805		

Volts

1000

800

600

400

10

50

90

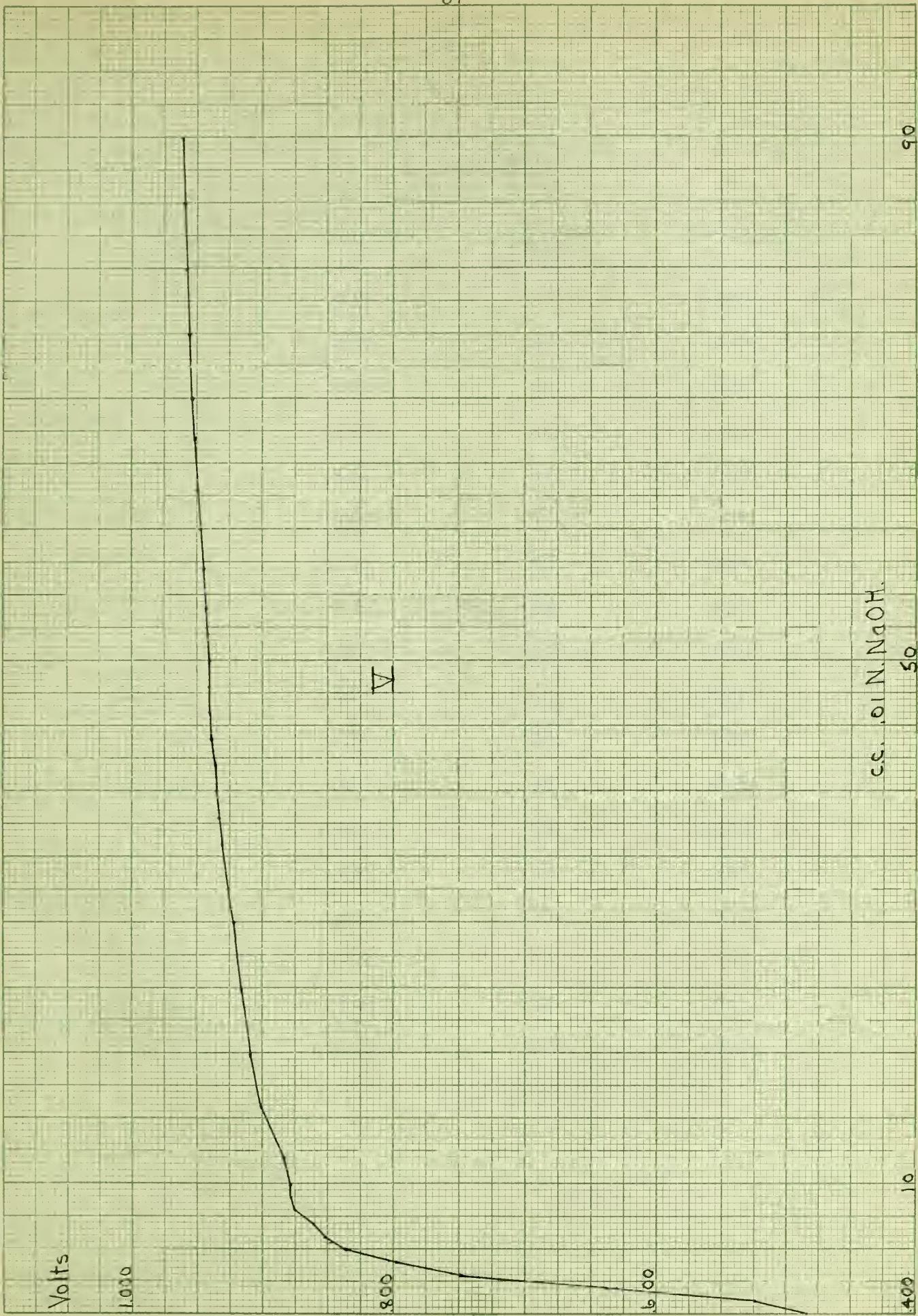
c.c. 01 N. NaOH

IV



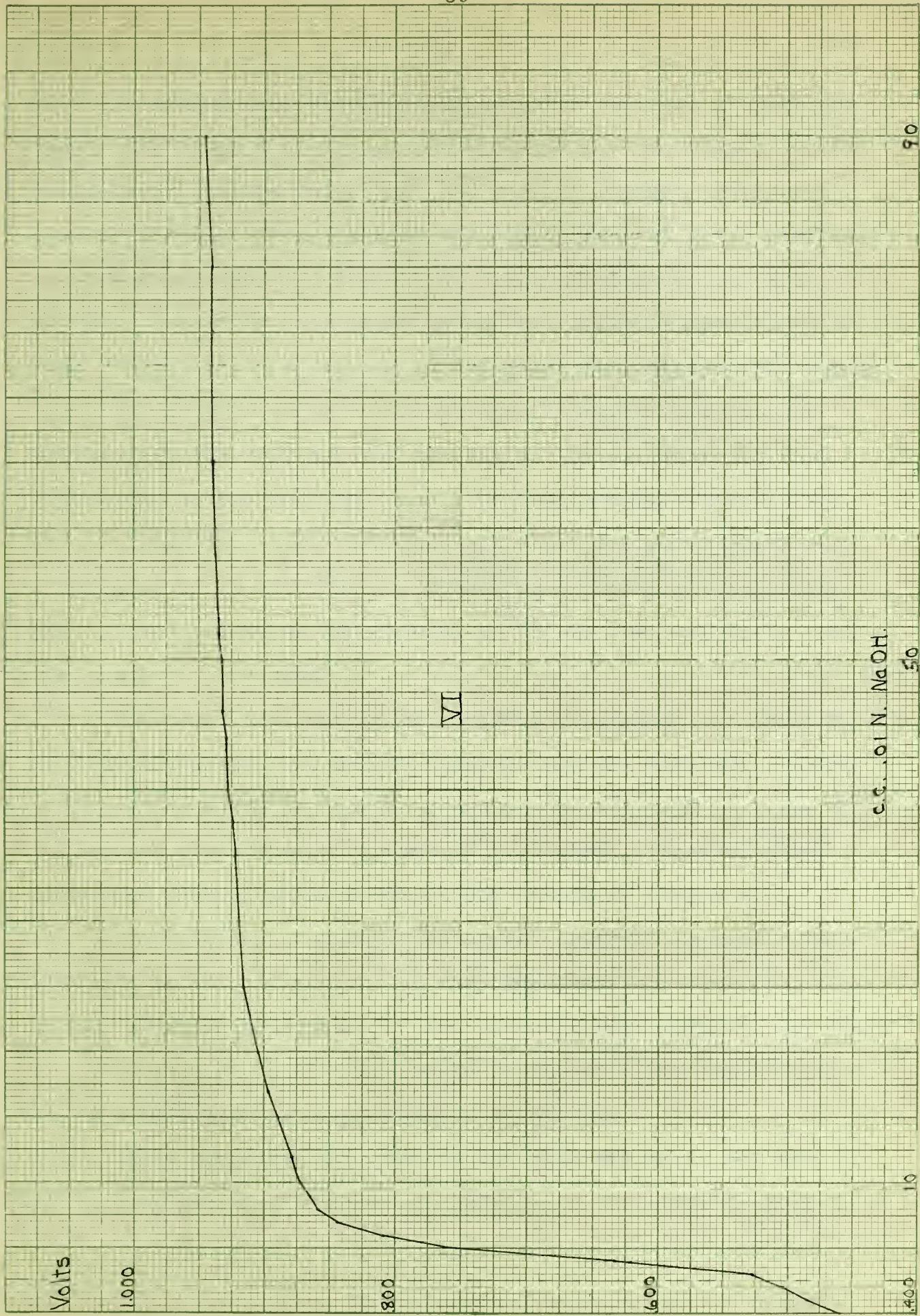
TITRATION V

Volume NaOH	Voltage	Volume NaOH	Voltage
0	.483	40	.934
1	.524	42	.936
2	.638	44	.938
3	.749	46	.940
4	.798	48	.940
5	.836	50	.940
6	.851	52	.941
7	.860	54	.943
8	.875	57	.945
9	.877	60	.947
10	.877	63	.949
12	.882	67	.951
16	.900	70	.953
20	.908	75	.955
25	.915	80	.957
30	.920	85	.959
36	.930	90	.960
38	.932		



TITRATION VI

Volume NaOH	Voltage	Volume NaOH	Voltage
0	.458	38	.922
1	.484	40	.926
2	.502	42	.926
3	.527	44	.926
4	.632	46	.930
5	.762	48	.930
6	.808	50	.931
7	.843	52	.933
8	.857	54	.934
9	.863	56	.935
10	.871	58	.936
12	.877	60	.937
15	.888	65	.938
17	.895	70	.938
20	.903	75	.939
25	.914	80	.940
30	.918	85	.941
35	.920	90	.943



I. In making this titration no definite interval of time was observed between the addition of the acid and the reading of the voltmeter. It was found that the voltage changed slowly for several minutes after the acid was added, so that these readings are not accurate. This is seen in the irregularity of the curve, although the inflection point shows an alkalinity very close to that determined by titrating in the usual way using methyl orange.

II. An interval of three minutes was observed between the addition of the acid and the reading of the voltmeter in this titration, so the readings should be more accurate than in the first titration. The inflection point on the curve shows the alkalinity to be the same as determined by using methyl orange.

III. This titration was carried on in the same way as II, and the result is the same.

IV. No definite interval was observed in making the readings in this titration, and so the readings are not accurate. When plotted, the curve is rather irregular and although it gives an inflection point when the solution is neutral, there is none where the precipitation of magnesium should be complete.

V. An interval of three minutes was observed in making the readings in this titration, so they should be more accurate than in the previous titration. The curve is more regular, but there is no inflection point which could be taken as the point between the precipitation of magnesium and of calcium.

VI. This titration was made in the same way as V, and the curve obtained by plotting the readings is very similar to V.

The water used in these titrations contained 30.7 p.p.m. of magnesium, and this would require 12.62 cc. of the NaOH solution to precipitate it..

CONCLUSION

The absence of any inflection point here favors the opinion that there is no clear cut division between the precipitation of magnesium and of calcium, but that in the quantities present the precipitations overlap. Not enough work has been done on this to say that magnesium could not be determined in this way, but conditions would have to be regulated more than is possible for a general laboratory method, and the results would not be any more accurate than those obtained by the usual gravimetric method. More time would be required also, and no time would be saved by making a number of determinations at the same time.

The results obtained from the titration with sulphuric are very satisfactory, giving the same result as the usual titration with methyl orange. More time is required however, so that the methyl orange method is preferable.





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